(5) 930700

8/

AD No. 423996

Technical Report No. 44

to the

OFFICE OF NAVAL RESEARCH
ARPA Order No. 26-60, Task 2, Item 3
Contract No.: Nonr - 477 (16)

(6)

THE PREPARATION AND PROPERTIES OF TRIFLUOROMETHOXY SULFURPENTAFLUORIDE, CF_3OSF_5, AND CIS-BIS (TRIFLUOROMETHOXY) TETRAFLUOROSULFUR (VI), $(CF_3O)_2SF_4$,

(10) by

Leonard C. Duncan and George H. Cady.

Department of Chemistry
University of Washington
Seattle 5, Washington

1963

NO OTS

(Contribution from the Department of Chemistry,
University of Washington)

THE PREPARATION AND PROPERTIES OF TRIFLUOROMETHOXY SULFURPENTAFLUORIDE CF_3OSF_5 AND CIS-BIS(TRIFLUOROMETHOXY)TETRAFLUOROSULFUR(VI) $(CF_3O)_2SF_4$

by

Leonard C. Duncan[1] and George H. Cady

ABSTRACT

Trifluoromethoxy sulfurpentafluoride and cis-bis(trifluoromethoxy)tetrafluorosulfur(VI) were prepared by the ultraviolet irradiation of gaseous mixtures of SF_4 with either CF_3OF or CF_3OOCF_3. The products have been characterized, and the structures confirmed by mass, infrared and nuclear magnetic resonance spectra.

21

(1) Presented at the Northwest Regional Meeting of the American Chemical Society, June 20, 1962.

Trifluoromethyl hypofluorite can be added across double bonds with cleavage at the O-F bond to yield, in the case of ethylene $CF_3OCH_2CH_2F$ [2,3], and in the case of carbonyl

---

(2) G. H. Cady, Abstracts, XVII International Congress of Pure and Applied Chemistry.

(3) J. A. C. Allison and G. H. Cady, J. Amer. Chem. Soc., 81, 1089 (1959).

---

fluoride, CF_3OOCF_3 [4]. It has now been found that trifluoro-

---

(4) R. S. Porter and G. H. Cady, *ibid.*, 79, 5628 (1957).

---

methyl hypofluorite also can be added to sulfur tetrafluoride to give trifluoromethoxy sulfurpentafluoride [5]. Cis-bis(tri-

---

(5) This compound has been reported by G. Pass and H. L. Roberts, Inorg. Chem. 2, 1016 (1963).

---

fluoromethoxy)tetrafluorosulfur (VI) is also produced.

EXPERIMENTAL

Materials - Trifluoromethyl hypofluorite [6] was

---

(6) K. B. Kellogg and G. H. Cady, J. Amer. Chem. Soc., 70, 3986 (1948).

---

obtained as the product of a flow reaction of carbon monoxide and fluorine at 350°C. Bis-trifluoromethyl peroxide [4] was prepared by passing streams of fluorine and carbon monoxide through a "catylitic" flow reactor [6] with the flow rates: 4 l/hr. F_2 and 2.7 l/hr. CO. The products of this reaction were collected in a trap held at -183°. The peroxide was refined by pumping the product mixture under vacuum through a train consisting of: (1) a .75 m length of 30 mm tubing packed with granulated soda lime, (2) a trap held at -78°, and (3) a trap held at -185°. The F_2, CF_3OF, CO_2, and COF_2 present in the crude material were absorbed by the soda lime. The water and oxygen formed in the soda lime column, along with CF_3OOCF_3 and CF_4, then passed through the trap at -78° where water was condensed, then to the trap at -183° where the peroxide was deposited while the CF_4 and O_2 present passed on to the vacuum pump. The CF_3OOCF_3 obtained in this manner was used without further purification. Sulfur tetrafluoride was supplied by E. I. du Pont de Nemours and Co., Inc. and was used directly from the cylinder.

Reactions - Equimolar amounts of gaseous CF_3OF and SF_4 were introduced into a three-liter Pyrex bulb to a total pressure of 252 mm. A quartz glass finger containing a water cooled Hanau 4.5 watt mercury arc lamp projected u.v. light into the bulb. After irradiation for three days the volatile products were condensed, and separated by fractional codistilation [7]. They were, in order of decreasing volatility,

(7) G. H. Cady and D. P. Siegwarth, Anal. Chem., 31, 618 (1959).

CF_3OF, SiF_4, COF_2, SO_2F_2, SOF_2, CF_3OOCF_3, CF_3OSF_5, $(CF_3O)_2SF_4$, and a small amount of a still less volatile material which was not identified. All of the above substances, except the last three, were identified by their characteristic infrared spectra. The yield of CF_3OSF_5 was approximately 10%, and that of $(CF_3O)_2SF_4$ about 8% of that theoretically possible from the amount of SF_4 used.

A mixture of equimolar amounts of CF_3OF and SF_4, with a total pressure of 408 mm was heated in a 1.5 l. nickel reactor which has been previously described [8]. The pressure was

(8) Wayne P. Van Meter and G. H. Cady, J. Amer. Chem. Soc., 82, 6005 (1960).

recorded at frequent temperature intervals and it was found that the pressure of the mixture increased in direct proportion to the absolute temperature up to 150°. Above this temperature the pressure vs. temperature curve "flattened", indicating a reaction which caused a decrease in the number of molecules. The product contained CF_3OSF_5 and $(CF_3O)_2SF_4$, but the yields were small.

The best yield (about 35%) of CF_3OSF_5 was obtained by the reaction of 2.5 g. of CF_3OF and 2.5 g. of SF_4 in a 5 cc Monel tube held at 100° for a week. The yield of $(CF_3O)_2SF_4$ was negligible in this case.

CF_3OSF_5 and $(CF_3O)_2SF_4$ were both obtained in about 10% yields from the ultraviolet irradiation, at room temperature, of an equimolar gaseous mixture of CF_3OOCF_3 and SF_4 with a total pressure of 500 mm in a 3 l. vessel.

General methods - Infrared spectra were studied using a Perkin-Elmer Model 21 Infrared Spectrometer with a sodium chloride prism. The gaseous samples were contained in a 10 cm glass cell with silver chloride windows. N.M.R. spectra were obtained through the use of a Varian Model 4311B high resolution spectrometer with a 40 megacycle oscillator. Mass spectra were recorded using a Consolidated Engineering Corporation type 21-103 mass spectrometer. Vapor densities were determined using a glass bulb of 258 ml. volume. Liquid densities were found using a single capillary pycnometer. Melting points were obtained by warming the solids slowly in a closed 5 mm o.d. Pyrex tube contained in a cold iso-pentane bath. Vapor pressures were determined using a method previously described [6].

Properties of trifluoromethoxy sulfurpentafluoride - Experimental measurements gave an average molecular weight of 213.4 compared to a molecular weight of 212.1 calculated for CF_3OSF_5. The density of liquid CF_3OSF_5, as determined at five temperatures in the range -30° to -5° (see table (1)) gave an extrapolated density at 0° of 1.772 g/cc, and a volume coefficient of expansion at 0° of 2.32 × 10^{-3}. The observed melting point was -143.0 ± .5°C. Vapor pressures, shown in Table 2, indicated a boiling point of -11.0°, a molar heat of vaporization of 5.84 kcal., and a Trouton constant of 22.3 e.u. The experimental data fit the expression $\log_{10} p_{mm} = \frac{-1.2757}{T} \times 10^3 + 7.7485$.

Table (1)

Densities of CF_3OSF_5

Temp. °	-29.5	-25.3	-19.5	-11.9	-4.5
Density, g/cc	1.889	1.872	1.851	1.821	1.790

Table (2)

Vapor Pressures of CF_3OSF_5

Pmm.	Temp. °K.	Pmm.	Temp. °K.
47.5	214.3	378.9	246.7
76.2	217.9	419.4	248.8
102.2	222.6	466.3	251.1
137.8	227.6	513.6	252.8
171.9	231.5	553.9	255.0
206.8	234.8	602.1	256.8
232.4	237.1	650.2	258.5
262.6	239.3	687.0	259.8
294.4	241.6	717.7	260.9
341.0	244.3	754.4	262.0
		(760.0)	(262.2)

The infrared spectrum at 2 and 10 mm, contained strong bands at 1275 cm^{-1} (7.84μ), 1238 cm^{-1} (8.07μ), and 1198 cm^{-1} (8.34 μ) due to the CF_3-O group. The strong bands at 934 cm^{-1} (10.70μ) and at 854 cm^{-1} (11.70μ) were attributed to the SF_5- group. L. H. Cross, et al [9] have shown

---

(9) L. H. Cross, G. Cushing, and H. L. Roberts, Spectro. Chem. Acta., 17, 344 (1961).

---

that in compounds containing the SF_5- group, intense absorption bands occur in the region from 850 to 920 cm^{-1}, and W. A. Sheppard [10] has found that the lower limit of this region may be

---

(10) W. A. Sheppard, J. Amer. Chem. Soc., 84, 3064 (1962).

---

extended to 820 cm^{-1}. It appears from the spectrum of CF_3OSF_5 that the upper limit of this region must be extended to at least 935 cm^{-1}. It is believed that the strong band at 698 cm^{-1} (14.30μ) is also due to the SF_5 group. This band is within the $-SF_5$ absorption region 706 cm^{-1} for SF_5Cl[9] and 690 cm^{-1} for SF_5Br[11]. The weak band centered at 759 cm^{-1} (13.16μ), and the

---

(11) C. I. Merrill and G. H. Cady, to be published.

---

strong band at 990 cm^{-1} (10.10 μ) were not assigned. The mass spectrum of CF_3OSF_5 above mass number 44 included in order of decreasing intensity, the following ions: SF_5^+, CF_3^+, SOF_3^+, COF^+, SF_3^+, SF_2^+, SF^+, SOF^+, $S^{34}F_5^+$, and SF_4^+. The nuclear magnetic resonance spectrum of this compound has been shown in another publication[12] to be that expected for the structure CF_3OSF_5.

(12) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. Eggers, J J. Inorg. Chem., 1, 215 (1962).

Trifluoromethoxy sulfurpentafluoride is colorless and low in reactivity as might be expected from its similarity to a saturated perfluoro ether [13]. The analysis was accomplished

(13) A. M. Lovelace, D. A. Raush, W. Postelnek, "Aliphatic Fluorine Compounds", American Chemical Society Monograph Series 138, Reinhold Publishing Co. New York, New York 1958.

on the products of the fusion of a known quantity of the compound with an excess of sodium. Found: sulfur 15.0%, Fluorine 70.2%. Theoretical: sulfur 15.1%, fluorine 71.2%.

Properties of cis-bis(trifluoromethoxy)tetrafluoro-sulfur (VI) - Molecular weight determinations gave an average value of 278.2 (theoretical, 278.1). Densities at four temperatures shown in Table 3 correspond to a volume coefficient of expansion at 0° of 1.85×10^{-3}.

Table (3)

Densities of $(CF_3O)_2SF_4$

Temp. °	0.0	9.7	20.2	35.2
Density g/cc	1.851	1.818	1.781	1.732

The melting point of this compound was not found. In all attempts the material became a glass when cooled below -130°. Vapor pressures shown in table (4) indicate a heat of vaporization of 6.89 kcal/mole, a normal boiling point of 29.1°, and a Trouton constant of 22.8 e.u. The data fit the expression $\log_{10}P_{mm} = \frac{-1.5061}{T} \times 10^3 + 7.8661$.

Table (4)

Vapor Pressures of $(CF_3O)_2SF_4$

Pmm	Temp. °K.	Pmm	Temp. °K.
52.8	246.1	449.5	288.9
107.6	258.5	407.4	291.8
137.6	263.2	537.5	293.4
171.9	267.4	574.8	295.1
214.1	272.1	607.4	296.5
250.2	275.5	647.2	298.2
281.9	278.1	681.4	299.4
308.8	280.1	706.6	300.5
339.2	282.2	736.9	301.6
375.0	284.6	750.2	302.0
413.6	286.7	(760.0)	(302.2)

The infrared spectrum of $(CF_3O)_2SF_4$ had strong bands at 1273 cm^{-1} (7.85μ), 1242 cm^{-1} (8.05μ), and 1146 cm^{-1} due to the CF_3O group. The strong absorptions at 935 cm^{-1} (10.69μ), 840 cm^{-1} (11.89μ), and 712 cm^{-1} (14.03μ) were attributed to the SF_4 group. Another strong absorption occurred at 972 cm^{-1} (10.28μ). The mass spectrum was due to the following ions, in order of decreasing intensity: CF_3^+, SOF_3^+, SF_3^+, SF_2^+, SOF^+, $S^{34}F_3^+$, SOF_2^+, COF_2^+, and SF_5^+. The SF_5^+ peak, mass 127, was weak in relative intensity, and was attributed to a trace impurity of CF_3OSF_5 in this sample.

The compound is colorless and does not react with water at room temperature. A sample stored over a 10 M. sodium hydroxide solution for three months showed no reaction, and another sample showed no change on being contacted with calcium at 100° for an hour. The analysis was carried out on the products of the reaction of this material with molten potassium. Found: sulfur 11.6%, fluorine 67.8%. Theoretical: sulfur 11.5%, fluorine 68.3%. The F^{19} n.m.r. spectrum of cis-bis(trifluoromethoxy)tetrafluorosulfur(VI) at 40 megacycles was studied. The part of the spectrum due to F atoms bound to the sulfur is a symmetrical group of fourteen bands, each of which is split seven times. If, in this molecule, the trifluoromethoxy groups were trans, all of the SF_4 fluorine atoms would be equivalent, yielding a single resonance, split seven times by the six neighboring CF_3 fluorines. It is evident from this spectrum that the two trifluoromethoxy groups must be in a cis configuration [14], giving rise to two different

(14) Jean'ne M. Shreeve and G. H. Cady, J. Amer. Chem. Soc., 83, 4524 (1961).

pairs of fluorine atoms bound to the sulfur. In order to show that the experimental spectrum was actually that of a cis-disubstituted derivative of SF_6, a theoretical spectrum was calculated for an A_2B_2 model using a generalized seven spin n.m.r. program[15]. It was found that the computed spectrum could be

(15) Program provided by K. B. Wiberg

matched to the experimental SF_4 portion of the spectrum using a chemical shift $\Delta\nu$ of 155.3 cps (3.88 ppm) and a spin coupling constant J_1 of 146.0 cps. The CF_3 portion of the spectrum was shifted $\Delta\nu$ = 5,700 cps (1425 ppm) to higher field strength. Spin coupling constants between the CF and SF atoms were J_2 = 7 cps and J_3 = 9 cps.

It is interesting, that in this case of "addition" of CF_3OOCF_3 to sulfur tetrafluoride, exclusively the cis-product is formed. This cis-configuration has also been shown to be preferred orientation in the formation of tetrafluorobis-fluorosulfonato sulfur VI [14] and bis-(pentafluorosulfoxo) sulfurtetrafluoride.[16]

(16) C. I. Merrill and G. H. Cady, J. Amer. Chem. Soc., <u>85</u>, 912 (1963).